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(54) PNEU DONT LES FLANCS DE CAOUTCHOUC CONTIENNENT DU CAOUTCHOUC RECYCLE
 (54) TIRE WITH RUBBER SIDEWALL CONTAINING RECYCLED RUBBER

(57)

A pneumatic rubber tire having a rubber sidewall composition containing recycled rubber, at least one additional rubber and tetrathiodipropionic acid.



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(54) **PNEU DONT LES FLANCS DE CAOUTCHOUC CONTIENNENT
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Industrie Canada Industry Canada

Abstract of the Disclosure

TIRE WITH RUBBER SIDEWALL CONTAINING RECYCLED RUBBER

5 A pneumatic rubber tire having a rubber sidewall composition containing recycled rubber, at least one additional rubber and tetrathiodipropionic acid.

TIRE WITH RUBBER SIDEWALL CONTAINING RECYCLED RUBBERField

5 This invention relates to a pneumatic rubber tire having a rubber sidewall composition. More specifically, the invention relates to such a tire having a rubber sidewall composition of a rubber blend containing recycled rubber.

10 Background of the Invention

It is often desired to reclaim or recycle vulcanized rubber. The vulcanized rubber is generally in the form of a manufactured article such as a pneumatic tire, industrial conveyor or power 15 transmissions belt, hose and the like. Scrap pneumatic tires are an especially large source of such vulcanized rubber.

The vulcanized rubber is conventionally broken down and reclaimed or recycled by various processes, 20 or combination of processes, which may include physical breakdown, grinding, chemical breakdown, devulcanization and/or cryogenic grinding. If the vulcanized rubber contains wire or textile fiber reinforcement, then it is generally removed by various 25 processes which might include a magnetic separation, air aspiration and/or air flotation step.

In this description, the terms "recycle" and "recycled rubber" are used somewhat interchangeably and relate to both vulcanized and devulcanized rubber 30 which is more completely hereinafter described. It is important to appreciate that devulcanized recycle or recycled rubber (sometimes referred to as reclaim rubber) relates to rubber which had been vulcanized and ground and may be followed by being substantially 35 or partially devulcanized.

The resultant ground recycle rubber is a polymeric material which has somewhat the appearance of unvulcanized rubber but has important differences and properties therefrom. First, it is a rubber which 5 is composed of a mixture of polymer units of various and numerous constructions different from either unvulcanized or vulcanized rubber.

Secondly, the recycled rubber, unlike conventional unvulcanized rubber, is also a complex 10 mixture of largely unknown polymer(s), of compounding ingredients, possibly bits of textile fiber, and the like.

It has been observed that, after adding sulfur and accelerator to recycle rubber, followed by its 15 revulcanization, the resulting physical properties, such as tensile and elongation, are usually lower than the corresponding properties of the original vulcanized rubber from which it was derived. It has also sometimes been observed that exposed edges of 20 bales or slabs of recycle rubber have tended to curl up, apparently a result of oxidation degradation which was probably due to a deficiency of antidegradants which would normally have been adequately present in unvulcanized, compounded rubber.

25 Pneumatic rubber tires conventionally have rubber sidewalls which may be subject to considerable flexing and scuffing.

Sidewalls of rubber tires may age somewhat prematurely as a result of (i) weathering due to 30 atmospheric conditions, (ii) fatigue cracking due to continual flexing under operating conditions, and (iii) abrasion due to scuffing.

Rubber sidewall ageing due to weathering may be, for example, a result of exposure to ultraviolet 35 light, ozone and high humidity. Antidegradants are conventionally mixed with the sidewall rubber to

counteract such effects. Also, often low unsaturation rubbers such as halobutyl rubber and EPDMs are included in or mixed with the sidewall rubber for such purpose.

5 Fatigue cracking of the sidewall rubber is usually due to continual flexing of the tire sidewall as the tire is run under load at service conditions. Such cracking can first initiate and then can propagate, over time, sometimes to an extent that it
10 penetrates deeper into the tire sidewall and, in some cases, may even penetrate the supporting carcass plies. Due to the severe requirements placed on the rubber for use in a sidewall of a tire and the above undesirable properties associated with use of recycled
15 rubber, recycled rubber has not been considered practical for use in a sidewall.

Summary of the Invention

The present invention relates to a pneumatic
20 rubber tire having a rubber sidewall composition containing recycled rubber and at least one additional rubber.

Detailed Description of the Invention

25 There is disclosed a pneumatic rubber tire having a rubber sidewall where said outer sidewall layer is a sulfur-cured rubber layer composition comprised of, (a) from about 5 to about 50 parts by weight of a recycled rubber which has an individual particle size
30 no greater than 420 microns; (b) from 0.1 to 5 parts by weight per 100 parts by weight of recycle rubber of 3,3'-tetrathiodipropionic acid; and (c) 100 parts by weight of at least one additional rubber selected from the group consisting of at least one of natural and/or
35 synthetic cis 1,4-polyisoprene rubber, cis 1,4-polybutadiene rubber, styrene/butadiene copolymer

rubber, styrene/isoprene/butadiene terpolymer rubber EPDM, acrylonitrile-butadiene rubber and 3,4-polyisoprene rubber.

In accordance with a preferred embodiment, the 5 pneumatic tire having a rubber sidewall, the outer layer is a sulfur-cured rubber composition comprised of 10 to 40 parts by weight of the recycled rubber and about 0.36 to 5 parts by weight per 100 parts by weight of recycled rubber of 3,3'-tetrathiodipropionic acid.

10 The recycle rubber should have a particle size no greater than 420 microns (40 mesh). Any particles greater than this render it impractical for subsequent mixing with the unvulcanized rubber. Generally 15 speaking, the individual particle size should have a particle size no greater than 250 microns (60 mesh) and preferably smaller than 177 microns (80 mesh). Preferably, the individual particle size ranges from 250 microns (60 mesh) to 74 microns (200 mesh).

20 The amount of tetrathiodipropionic acid is dependent on the amount of recycled rubber. Generally speaking, the amount of tetrathiodipropionic acid ranges from 0.10 to 5 parts by weight based on 100 parts by weight of recycled rubber. Preferably, the 25 level of tetrathiodipropionic acid that is dispersed ranges from 0.36 to 5.0 phr.

20 The tetrathiodipropionic acid may be added neat, dispersed directly on a carrier, on the recycle rubber or be suspended or dissolved in a solvent and thereafter applied to the recycled rubber or carrier, with subsequent solvent-stripping. Representative examples of such solvents include acetone, chloroform, dichloromethane, carbon tetrachloride, hexane, heptane, cyclohexane, xylene, benzene, 35 dichloroethylene, dioxane, diisopropyl ether,

tetrahydrofuran and toluene. Preferably, the solvent is acetone.

Representative carriers include carbon black or silica.

5 The recycled rubber having dispersed therein or thereon the tetrathiodipropionic acid is interchangeably referred to herein as "treated recycled rubber." The treated recycled rubber is mixed with additional rubber for use in the sidewall.

10 In the practice of this invention, the sidewall rubber composition is comprised of at least one rubber selected from cis 1,4-polyisoprene rubber, natural or synthetic, 3,4-polyisoprene rubber, styrene/butadiene copolymer rubbers, styrene/isoprene/butadiene 15 terpolymer rubbers, EPDM, butyl rubber, halobutyl rubber and cis 1,4-polybutadiene rubber. Preferably it is comprised of a combination of natural rubber or cis 1,4-polyisoprene rubber and cis 1,4-polybutadiene rubbers.

20 It is readily understood by those having skill in the art that the rubber compositions of the sidewall would be compounded by methods generally known in the rubber compounding art, such as mixing the various sulfur-vulcanizable constituent rubbers with various 25 commonly used additive materials such as, for example, curing aids, such as sulfur, activators, retarders and accelerators, processing additives, such as oils, resins including tackifying resins, silicas, and plasticizers, fillers, pigments, fatty acid, zinc 30 oxide, waxes, antioxidants and antiozonants, peptizing agents and reinforcing materials such as, for example, carbon black. As known to those skilled in the art, depending on the intended use of the sulfur vulcanizable and sulfur vulcanized material (rubbers), 35 the additives mentioned above are selected and commonly used in conventional amounts.

Typical additions of carbon black may comprise about 20 to 80 parts by weight per 100 parts by weight of diene rubber (phr), preferably 30 to 50 phr.

Typical amounts of tackifier resins, if used, may 5 comprise about 0.5 to about 10 phr, usually about 1 to about 5 phr. Typical amounts of processing aids may comprise 1 to 20 phr. Such processing aids can include, for example, aromatic, napthenic, and/or paraffinic processing oils. Silica, if used, may be 10 used in an amount of about 5 to about 25 phr, often with a silica coupling agent. Representative silicas may be, for example, hydrated amorphous silicas. Typical amounts of antioxidants comprise about 1 to 15 about 5 phr. Representative antioxidants may be, for example, diphenyl-p-phenylenediamine and others, such as, for example, those disclosed in the Vanderbilt Rubber Handbook (1978), pages 344-346.

Typical amounts of antiozonants comprise about 1 to 20 about 5 phr. Typical amounts of fatty acids, if used, which can include stearic acid comprise about 0.5 to about 3 phr. Typical amounts of zinc oxide comprise about 2 to about 6 phr. Typical amounts of waxes comprise about 1 to about 5 phr. Often microcrystalline waxes are used. Typical amounts of 25 peptizers comprise about 0.1 to about 1 phr. Typical peptizers may be, for example, pentachlorothiophenol and dibenzamidodiphenyl disulfide. The presence and relative amounts of the above additives are considered to be not an aspect of the present invention which is 30 more primarily directed to the utilization of specified blends of rubbers in tire sidewalls as sulfur vulcanizable compositions.

The vulcanization is conducted in the presence of 35 a sulfur vulcanizing agent. Examples of suitable sulfur vulcanizing agents include elemental sulfur (free sulfur) or sulfur donating vulcanizing agents,

for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts. Preferably, the sulfur vulcanizing agent is elemental sulfur. As known to those skilled in the art, sulfur vulcanizing agents 5 are used in an amount ranging from about 0.5 to about 4 phr, with a range of from about 0.5 to about 2.25 being preferred.

Accelerators are used to control the time and/or temperature required for vulcanization and to improve 10 the properties of the vulcanizate. In one embodiment, a single accelerator system may be used, i.e., primary accelerator. Conventionally, a primary accelerator is used in amounts ranging from about 0.5 to about 2.0 phr. In another embodiment, combinations of two or 15 more accelerators which the primary accelerator is generally used in the larger amount (0.5 to 2 phr), and a secondary accelerator which is generally used in smaller amounts (0.05-0.50 phr) in order to activate and to improve the properties of the vulcanizate. 20 Combinations of these accelerators have been known to produce a synergistic effect on the final properties and are somewhat better than those produced by use of either accelerator alone. In addition, delayed action accelerators may be used which are not affected by 25 normal processing temperatures but produce satisfactory cures at ordinary vulcanization temperatures. Suitable types of accelerators that may be used in the present invention are amines, disulfides, guanidines, thioureas, thiazoles, 30 thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound. The presence and 35 relative amounts of sulfur vulcanizing agent and accelerator(s) are not considered to be an aspect of

this invention which is more primarily directed to the utilization of specified blends of rubbers in tire sidewalls, particularly the inclusion of the trans polybutadiene in the sidewalls.

5 Sometimes, the combination of zinc oxide, fatty acid, sulfur and accelerator(s) may be collectively referred to as curatives.

10 Sometimes a combination of antioxidants, antiozonants and waxes may be collectively referred to 10 as antidegradants.

The tire can be built, shaped, molded and cured by various methods which will be readily apparent to those having skill in such art.

15 The prepared tire of this invention is conventionally shaped and cured by methods known to those having skill in such art.

20 The invention may be better understood by reference to the following example in which the parts and percentages are by weight unless otherwise indicated.

Example 1

25 Eight rubber formulations were prepared to compare and contrast the importance of the use of ground recycled rubber and ground recycle rubber in combination with tetrathiodipropionic acid. Each rubber formulation contained 35 parts by weight of natural rubber and 65 parts by weight of Budene® 1207.

30 Budene® 1207 is a cis-polybutadiene rubber marketed by The Goodyear Tire & Rubber Company. Each rubber formulation also contained the same conventional amounts of processing oil, peptizer, fatty acids, antidegradants, waxes, zinc oxide, primary and secondary accelerators and sulfur. Each formulation 35 differed by the additional ingredients listed in Table

I. The rubber formulations were prepared in a two-stage Banbury™ mix. All parts and percentages are by weight unless otherwise stated. Samples 1-4 are Controls and Samples 5-8 represent the present 5 invention.

Cure properties were determined using a Monsanto oscillating disc rheometer which was operated at a temperature of 150°C and 100 cycles per minute. A description of oscillating disc rheometers can be 10 found in the Vanderbilt Rubber Handbook edited by Robert O. Ohm (Norwalk, Conn., R. T. Vanderbilt Company, Inc., 1990), pages 554-557. The use of this cure meter and standardized values read from the curve are specified in ASTM D-2084. A typical cure curve 15 obtained on an oscillating disc rheometer is shown on page 555 of the 1990 edition of the Vanderbilt Rubber Handbook.

In such an oscillating disc rheometer, compounded rubber samples are subjected to an oscillating 20 shearing action of constant amplitude. The torque of the oscillating disc embedded in the stock that is being tested that is required to oscillate the rotor at the vulcanization temperature is measured. The values obtained using this cure test are very 25 significant since changes in the rubber or the compounding recipe are very readily detected. It is obvious that it is normally advantageous to have a fast cure rate.

The following Table I reports cure properties 30 that were determined from cure curves that were obtained for the rubber stocks that were prepared. These properties include a torque minimum (Min. Torque), a torque maximum (Max. Torque), the difference between Max Torque and Min Torque (Delta 35 Torque), Final Torque (Final Torq). In addition, there is provided the property value for each sample

- 10 -

when cured for 6 minutes at 170°C and 19.5 minutes at 150°C.

TABLE I

Sample No.	Control 1	Control 2	Control 3	Control 4	5	6	7	8
Recycled Rubber	10	20	40	0	20	20	40	40
Tetraiodopropionic acid ¹	0	0	0	0	1	2	1	2
ODR-100S Cmptn (20) Temp 150°C								
Min Torq	8.39	8.85	9.71	7.85	8.80	8.85	9.82	10.14
Max Torq	24.61	23.75	22.15	25.20	28.30	30.76	26.45	29.07
Delta Torq	16.22	14.90	12.44	17.36	19.50	21.92	16.64	18.93
Final Torq	24.52	23.38	22.11	24.61	27.85	30.40	26.04	28.70
Stress/Strain 6 min/170°C								
Mod 100	0.98	0.90	0.81	1.04	1.29	1.38	1.14	1.29
Mod 150	1.40	1.27	1.12	1.50	1.92	2.09	1.67	1.93
Mod 200	2.02	1.83	1.58	2.21	2.84	3.12	2.46	2.88
Mod 300	3.92	3.55	3.08	4.30	5.42	5.96	4.78	5.55
Tensile	11.02	9.15	7.11	11.71	12.35	12.66	10.27	11.28
Elongation	657	594	535	651	584	568	540	531
Energy, J	94.14	67.21	46.00	102.44	96.85	100.38	73.83	83.26
Static Ozone 40°C 0.5 ppm ozone								
Average ²	2.5/70	2.5/70	3.5/70	2/65	2/75	2/70	3.5/85	3.5/85
Cyclic Ozone - 21 days 40°C 0.5 ppm ozone 25% extension								
Average ²	1/95	2/100	2/100	1/85	E	0/0	0/0	0/0

TABLE I (cont'd)

Sample No.	Control 1	Control 2	Control 3	Control 4	5	6	7	8
Hardness at RT	44.0	42.3	40.2	45.1	48.2	51.0	47.3	50.0
Hardness at 100	40.5	38.6	35.6	42.1	44.9	47.5	42.9	45.8
Rebound at RT	50.8	49.1	47.1	53.2	54.4	55.8	51.0	52.9
Rebound at 100	55.1	52.9	49.7	58.0	58.8	60.5	55.2	57.4
Spec Grav	1.095	1.096	1.098	1.089	1.095	1.099	1.100	1.101
Stress/Strain 19.5 min/150°C								
Mod 100	1.12	1.07	0.99	1.17	1.46	1.64	1.31	1.51
Mod 150	1.63	1.53	1.40	1.71	2.20	2.54	1.96	2.33
Mod 200	2.39	2.23	2.02	2.52	3.27	3.81	2.91	3.50
Mod 300	4.59	4.31	3.96	4.84	6.17	7.12	5.63	6.66
Tensile	12.60	11.06	9.04	13.45	12.81	13.26	11.50	12.58
Elongation	663	611	550	678	562	522	534	514
Energy, J	112.80	85.34	61.53	122.35	99.04	94.76	83.16	90.10
Hardness at RT	46.4	45.5	43.3	46.4	50.3	53.2	49.3	52.2
Hardness @ 100°C	42.7	41.3	38.4	43.6	47.2	49.8	45.1	47.7
Rebound at RT	52.6	51.1	49.3	55.0	56.0	57.8	52.8	54.9
Rebound @ 100°C	57.0	54.7	51.4	60.0	60.2	62.6	57.1	59.2

¹Tetrathiiodipropionic acid dispersed on carbon black in a weight ratio of 1:1.

²Size of cracks/% of surface with cracks. Size 5 is based on 0-10 scale with 0 being lowest. E is edge only.

Controls 1 through 3 which contain varied levels of recycle rubber and no tetrasulfide show a 10 directional decrease in state-of-cure (Delta Torq), loss in compound stiffness (Mod 300), loss in tensile strength, hardness and in rebound as the level of recycle rubber increases versus the Control 4 which contains no recycle or tetrasulfide, all of which were 15 cured at ATS cure of 6 minutes at 170°C. Loss of these properties, such as state-of-cure, hardness and Mod 300 stiffness will give a tire without sufficient durability to be practical. Also, the loss in tensile strength and rebound will produce a tire with 20 unacceptable hysteresis and heat buildup. Controls 5 and 6 with 20 parts of recycle rubber show a dramatic increase in state-of-cure (Delta Torq), stiffness (Mod 300), tensile strength, hardness and rebound when 1 or 2 parts of the supported tetrasulfide is present under 25 the same cure conditions. Controls 5 and 6 show that any lost property of Control 4, as shown in Controls 1, 2 and 3, are readily retained plus increased values. Controls 7 and 8 with a higher level of recycle rubber show that 1 part of tetrasulfide cannot 30 fully retain the properties of Control 4, but two parts of tetrasulfide in Control 8 gives practically the same values of Control 4 with no recycle rubber. ATS cure at 19.5 minutes at 150°C gives high modulus (stiffness) for all Controls 5 through 8 with 35 tetrasulfide.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and 5 modifications may be made therein without departing from the spirit or scope of the invention.

WHAT IS CLAIMED IS:

1. A pneumatic rubber tire is provided having a rubber sidewall where said outer layer is a sulfur cured rubber composition comprised of (a) from about 5 to about 50 parts by weight of a recycled rubber which has an individual particle size no greater than 420 microns, (b) from 0.1 to 5 parts by weight per 100 parts by weight of recycled rubber, of 3,3'-tetrathiodipropionic acid; and (c) 100 parts by weight of at least one additional rubber selected from the group consisting of natural rubber, synthetic cis 1,4-polyisoprene rubber, cis 1,4-polybutadiene rubber, styrene/butadiene copolymer rubber, styrene/isoprene/butadiene terpolymer rubber, EPDM, acrylonitrile-butadiene rubber and 3,4-polyisoprene rubber.
2. The tire of claim 1 wherein said outer sidewall layer is comprised of from (a) about 10 to about 40 parts by weight of said recycled rubber and about 0.36 to about 5.0 parts by weight of 3,3'-tetrathiodipropionic acid.
3. The pneumatic tire of claim 1 wherein the 3,3'-tetrathiodipropionic acid is predispersed in the recycled rubber.
4. The pneumatic tire of claim 1 wherein the 3,3'-tetrathiodipropionic acid is predispersed or carbon black.
5. The pneumatic tire of claim 1 wherein the 3,3'-tetrathiodipropionic acid is added neat.

6. The pneumatic tire of claim 1 wherein the 3,3'-tetrathiodipropionic acid is dispersed in a solvent prior to being homogeneously dispersed in said recycled rubber with subsequent solvent-stripping.

5

7. The pneumatic tire of claim 6 wherein said solvent is selected from the group consisting of acetone, chloroform, dichloromethane, carbon tetrachloride, hexane, heptane, cyclohexane, xylene, 10 benzene, dichloroethylene, dioxane, diisopropyl ether, tetrahydrofuran and toluene.

8. The pneumatic tire of claim 6 wherein said solvent is acetone.

15

9. The pneumatic tire of claim 1 wherein the particle size is no greater than 250 microns.

10. The pneumatic tire of claim 1 wherein the 20 particle size ranges from 250 microns to 74 microns.

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